



Stable Blue Photoluminescence from Porous Silicon

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Blue emission from porous silicon is realized that is stable and clearly visible to naked eyes even after two months' exposure in ambient air. The porous silicon is formed by the usual anodization with the aid of an oxidative metal but without any post-anodization treatment. The origin of this photoluminescence is revealed and interpreted in terms of formation of interfacial oxide-related defects followed by passivation by oxygen.

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Since the observation of intense photoluminescence (PL) from porous silicon (PS) at room temperature,¹ various methods have been used to form efficient blue-emitting PS.²⁻⁷ Two main approaches have been taken to achieve the blue luminescence from PS. One is based on oxidation such as rapid thermal annealing,² wet treatment,³ or photoinduced oxidation by filtered⁴ or UV⁵ light illumination. The other is based on photoinduced etching of as-prepared PS by white light in open circuit conditions.^{6,7} In the oxidation method, an oxidation step is needed to obtain the blue-emitting PS. This requirement is an evidence that some oxide-related defects are associated with the blue emission mechanism. On the other hand, in the photoinduced etching method, the PS samples with tuned spectra from green to blue do not show any sign of growth of the surface oxide.^{6,7} This apparent discrepancy can only be explained by different luminescent mechanisms of blue PS. It may be that the former is related to the oxide-related defects while the latter is associated with the quantum-confined nanostructures.

There have been two main problems in blue luminescence. First, the intensity of the blue emission is very weak and not detectable to naked eyes.²⁻⁷ Second, the blue emission is very unstable and disappears immediately after it is exposed to air, especially in the photoinduced etching method.^{6,7} Production of a strong photoluminescence that is stable in air has, so far, been unsuccessful.

In this work, we report blue PL from PS that is stable and visible to naked eyes even after two months' exposure in ambient air. The PS was formed using the method reported earlier⁸ where it had been shown that blue-to-red PL can be realized by simply changing the current density in electrochemical etching when an "oxidative" metal is used in the etching solution. A metal is termed oxidative here in the sense that its reduction potential is lower than hydrogen.

Experimental

The PS samples were prepared using 1-10 Ω cm p-type Si(100) wafers by electrochemical etching at a constant density of 100 mA/cm². Aluminum was sputtered onto the back side of the wafer for ohmic contact. The electrolyte was 20 vol % HF (50% by weight), 30% methanol, and 50% deionized (DI) water. An oxidative metal such as Zn or Fe was dissolved in the electrolyte solution in excessive amounts, typically 10⁻³ mol/L, to saturation. The etching time was 5 min. After the anodization, the sample was rinsed in DI water and blow-dried by nitrogen.

The sample was analyzed by PL and transmittance Fourier transform infrared (FTIR) spectroscopies. The PL spectra were measured by the third harmonic of a Spectra-Physics Q switched Nd:YAG laser (wavelength 355 nm). The pulse width produced by this laser is about 7 ns and the energy of laser is 1-2 mJ/pulse. A 360 nm filter was used in the illumination. The PL was detected by a Hamamatsu photomultiplier tube (PMT) and the signals were then summed and averaged using a boxcar averager (Stanford Research Systems).

Results and Discussion

Ambient room temperature PL spectra of an as-prepared sample are shown in Fig. 1 that had been taken over a period of two months. The inset shows the peak intensity as a function of aging time in air. The intensity reduces to about 60% of the initial intensity in about 20 days but the intensity stays almost the same thereafter. The blue emission is very strong and visible to naked eyes even after two months in air. The spectrum is relatively sharp and the peak position is located at about 430 nm. The PL spectra of the aged sample do not show much change with time. However, the half-width gets smaller in the first twenty days but does not change much thereafter. To check whether the blue emission is related to carbon contamination,⁹ the samples were rinsed in acetone for 1 h. However, the treatment did not degrade the luminescence. On the other hand, the luminescence quenched quickly when dipped in HF solution, which indicates that the blue emission is associated with oxide-related defects.

Figure 2 shows a deconvolution result of the PL spectrum of the as-prepared sample that was three days old, revealing that the spectrum consists of two Gaussian peaks. The first peak is located at 423 nm and the second at 489 nm. After 10 days' aging, the PL peak at 489 nm disappeared, and only the peak at 423 nm remained. The peak at 489 nm may be due to quantum confined nanostructure and therefore it disappeared after air exposure. On the other hand, the peak at 423 nm may result from oxide-related defects and therefore, it was very stable to ambient environment.

In order to investigate the nature of the blue emission, we checked the transmittance FTIR spectra of the freshly etched blue sample, which are shown in Fig. 3. For the sample prepared with an oxidative metal such as Zn or Fe, the peak intensity of the Si-O-Si stretching is relatively larger than that of the sample without metal

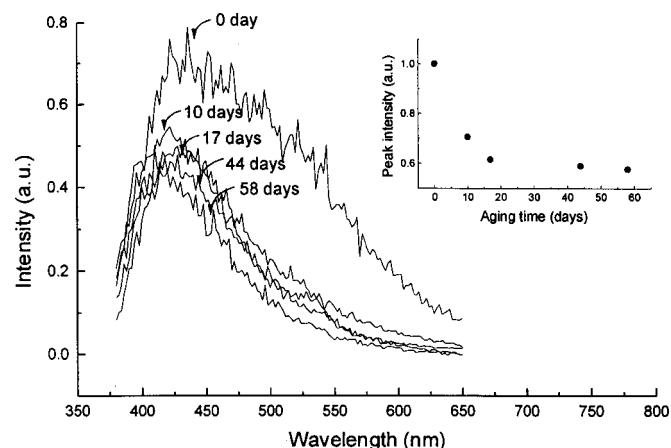


Figure 1. PL spectra of the blue-emitting PS fabricated by Zn-aided electrochemical etching. The inset shows normalized peak intensity as a function of aging time.

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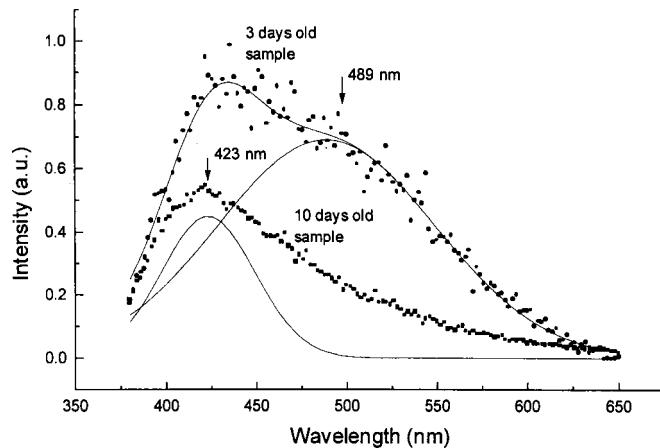


Figure 2. Deconvolution spectra of the PL spectrum from the PS left in air for three days that was fabricated by electrochemical etching with Zn. The spectrum after 10 days is also shown for comparison.

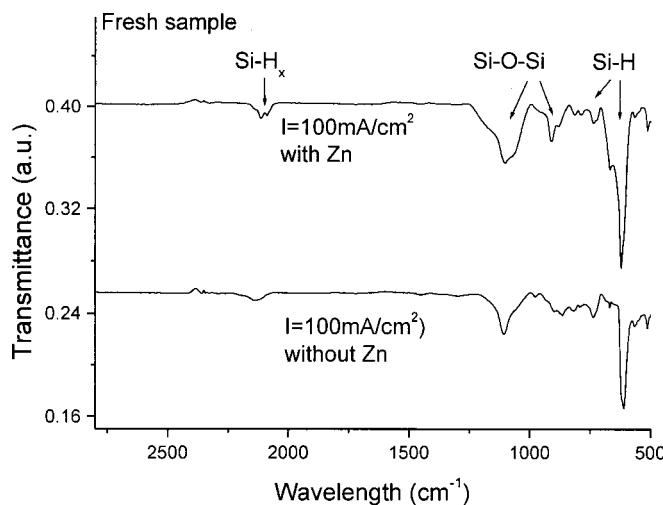


Figure 3. Transmittance FTIR spectrum of the Zn-aided PS sample prepared with $I = 100 \text{ mA/cm}^2$. The spectrum of the conventional porous silicon prepared with $I = 100 \text{ mA/cm}^2$ is also shown for comparison.

for the same solution composition (conventional PS). The peak of the antisymmetric stretching is split into two. It is noted that the integral intensity ratio of the AS₁ ($\sim 1080 \text{ cm}^{-1}$) to the AS₂ ($\sim 1200 \text{ cm}^{-1}$) peak of the antisymmetric stretching is larger for the metal-aided PS compared with the conventional PS. This fact reveals that the amorphous level and strain in the film is larger¹⁰ in the metal-aided PS. In this amorphous-like structure, many oxide-related defects may form and they are passivated with oxygen when exposed to air.

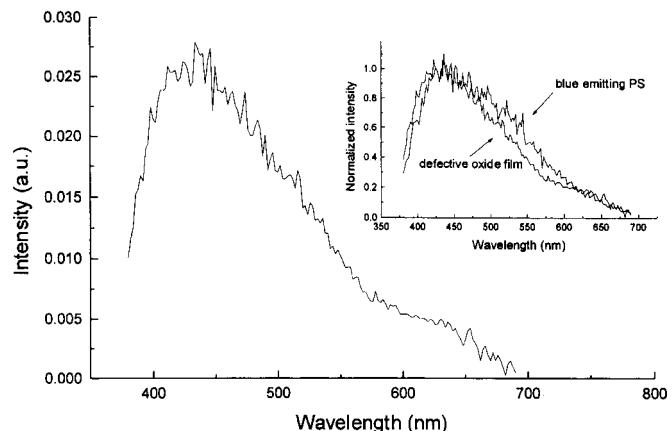


Figure 4. PL spectrum of the defective oxide film treated by oxygen plasma. The inset shows that the spectrum from the blue-emitting PS almost coincides with that from the defective oxide film when normalized.

The disappearance of the PL peak at 489 nm together with the FTIR result suggests that the blue emission could be from the oxide defects.

To test this hypothesis that the blue emission is due to the oxide-related defects, we prepared defective silicon oxide film by oxygen plasma treatment. In the course of the plasma treatment, many oxygen-induced defects formed in the oxide film. The spectrum of the photoluminescence from this oxide film is shown in Fig. 4. Although the PL intensity is very low, its peak and shape resemble those of the PL from the blue sample prepared by the metal-aided etching. In fact, the two spectra almost coincide as shown in the inset of Fig. 4, when they are superimposed by normalization for comparison. This result reveals that the PL emission of the two samples originates from the same source, which is oxide defects.

Conclusions

Bright blue emission from PS is realized that is stable even after a long exposure to ambient air. There are indirect evidences that the porous silicon owes its stability and intensity of the blue emission to well-formed oxygen-related defects that are passivated by oxygen in air. The nature of the blue emission may be associated with the oxide-related defects, which has been confirmed by the PL spectrum of the defective oxide film treated by oxygen plasma.

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